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On The Electronic Configuration in Pu

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MRS Proceedings: On the electronic configuration in Pu

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Abstract

Synchrotron-radiation-based x-ray absorption, electron energy-loss spectroscopy, and density-functional calculations have been used to study the electron configuration in Pu. These methods suggest a $5f^n$ configuration for Pu of $5 \leq n < 6$, with $n \neq 6$.

X-ray Absorption and Electron Energy Loss Spectroscopy

The data from x-ray absorption (XAS) and electron energy loss spectroscopy (EELS) indicate that the number of 5*f* electrons, *n*, involved in bonding of Pu must be at least as great as 5 and less than 6. The equivalence of the XAS and high-energy EELS measurements for assessing the electronic states has already been demonstrated for Ce and Pu, as well as for other actinides [1-5]. The argument against $n = 6$ will now be discussed in a step-wise fashion.

I. The relative diminishment of the Pu $4d_{3/2}$ peaks indicates strong relativistic effects in the Pu 5*f* states, i.e., a jj-coupling or jj-skewed intermediate coupling scheme.

As can be seen in Figure 1, the intensity of the $4d_{3/2}$ peak of Pu is significantly reduced versus that for U [6]. This large reduction is driven by the electric dipole selection rule that forbids the transition from a pure $d_{3/2}$ peak into a pure $f_{7/2}$ peak. This reduction also implies that the Pu 5*f* states must be split into two lobes, the lower (mainly occupied) lobe being principally pure 5/2 character and the upper (unoccupied) lobe being principally pure 7/2 character. This picture is shown schematically in Figure 2. This result is independent of any particular theoretical model for spin-orbit splitting or the calculation of x-ray absorption cross section and thus does *not* depend upon the details of the branching ratio analysis presented previously [1,4].

II. Coupled with the result in I above, the absence of a pre-peak in the Pu 5*d* XAS and EELS indicates that *n* must be at least 5.

As shown in Figure 3, there is a pre-peak in the EELS 5*d* to 5*f* transition for Th and U, but not for Pu. Similar results (Figure 4) have been obtained for 5*d* XAS. [2]. The pre-peak structure in the 4*d* XAS of the rare earths was explained many years ago by Dehmer *et al*. [7]: it is driven by the combination of angular momentum coupling between the 4*d* and 4*f* states and the dependence of the Coulombic energy term upon the coupling details. The spectroscopic transition for the rare earths can be summarized as follows.

$$4d^{10}4f^{n} + h\nu \rightarrow 4d^{9}4f^{n+1} \qquad \text{Eq A}$$

When $n = 14$, there is no transition. When $n = 13$, there is a single main peak, without any pre-peaks [2]. This is because partial occupation of both the *d* and *f* states is required for coupling. If $n = 13$ and $n + 1 = 14$, then in the final state the 4*f* level is filled and no coupling occurs. For the lighter actinides ($n < 6$), the situation is similar but not identical.

$5d_{5/2}$, pure jj, $n < 6$ Eq B1

$$(5d_{3/2})^4(5d_{5/2})^6(5f_{5/2})^n(5f_{7/2})^0 + h\nu \rightarrow (5d_{3/2})^4(5d_{5/2})^5(5f_{5/2})^{n+1}(5f_{7/2})^0 + (5d_{3/2})^4(5d_{5/2})^5(5f_{5/2})^n(5f_{7/2})^1$$

$5d_{3/2}$, pure jj, $n < 6$ Eq B2

$$(5d_{3/2})^4(5d_{5/2})^6(5f_{5/2})^n(5f_{7/2})^0 + h\nu \rightarrow (5d_{3/2})^3(5d_{5/2})^6(5f_{5/2})^{n+1}(5f_{7/2})^0$$

Again transitions from $d_{3/2}$ to $f_{7/2}$ are forbidden. For the pre-peaks at lower hν, we need only consider the $(5f_{5/2})^{n+1}$ terms. (Transitions into the $f_{7/2}$ states will generally need higher energies and pre-peaks that might be associated with this transition will be coincident with the main $f_{5/2}$ spectral structure and lost therein.) The final state 5/2 level will be filled at $n + 1 = 6$ or $n = 5$. For $n < 5$ (e.g., Th and U), there will be pre-peaks. The absence of pre-peaks for Pu, both the α and the δ phase, indicates that *n* must be 5 or greater. This raises the question: What about an *n* of 6 and above for Pu? For $n \geq 6$, the transition looks like this.

$5d_{5/2}$, pure jj, $n \geq 6$ Eq C1

$$(5d_{3/2})^4(5d_{5/2})^6(5f_{5/2})^6(5f_{7/2})^{n-6} + h\nu \rightarrow (5d_{3/2})^4(5d_{5/2})^5(5f_{5/2})^6(5f_{7/2})^{n-5}$$

$5d_{3/2}$, pure jj , $n \geq 6$ Eq C2

$$(5d_{3/2})^4(5d_{5/2})^6(5f_{5/2})^6(5f_{7/2})^{n-6} + h\nu \rightarrow$$ No Transition Allowed

Once again, there will be no transition in Eq C2 because $d_{3/2}$ to $f_{7/2}$ transitions are forbidden.

The situation is different in another, subtle way as well. A filled $5f_{5/2}$ level now stands between the partially occupied 5*d* and $5f_{7/2}$ levels. It is unclear whether angular momentum coupling (and thus pre-peak formation) will occur under these conditions. In fact, the spectrum from AmH_2 shown in Figure 3 exhibits no evidence of pre-peaks. Although this is not a spectrum from an elemental actinide, past experiments have shown that for a given actinide, the peak-ratio values tend to be grouped together, with larger separations between the elemental groups [8]. The grouping tended to be tightest for actinide elements that exhibited a strong localization even in the elemental, metallic state.

III. The presence of two edges in the Pu 5*d* XAS and a substantial peak in the $4d_{3/2}$ XAS indicate that $n < 6$.

As can be seen in the 5*d* XAS of both α- and δ-Pu (Figure 4), there are two strong edges for hν = 110 - 120 eV. A similar, albeit weaker, structure is observed in the EELS of α- and δ-Pu, as shown in Figure 3. These two steps are the leading edges of the main $5d_{5/2}$ (about 110 eV) and $5d_{3/2}$ (about 120 eV) transitions. (Confirmation of the initiation of the 5*d* transition near 110 eV can be gleaned from photoelectron spectroscopy. See Ref. 9 and references therein.) As illustrated in Eq C2, if $n = 6$ or more, one of the two transitions is lost. This is exactly what has happened in AmH_2, as shown in Figure 3. Here, the second spin-orbit split peak is essentially gone, or at least strongly attenuated, and lost in the tail of the other peak/edge. The overall peak

structure of the "giant resonance" of AmH_2 is now about half as wide as that of the Pu. Thus, the presence of two strong edges indicates that $n < 6$ for Pu.

An analogous process will occur for the 4*d* to 5*f* transitions. For a pure jj coupling scheme and electric dipole selection rules, the $4d_{3/2}$ peak should vanish. In reality, there will be mixing between the pure $5f_{5/2}$ and $5f_{7/2}$ states, so at $n = 6$, one would expect a small but almost negligible $4d_{3/2}$ peak. Again, this is exactly what has been observed for AmH_2 as shown in Figure 5 [8]. The Pu $4d_{3/2}$ peak is too large for $n = 6$, and therefore for Pu, $n < 6$.

What about the possibilities for Am being $n > 6$? This seems unlikely. As will be discussed below, there is very strong evidence that Am has $n = 6$. Additionally, recent measurements on Cm [10] indicate that $n = 7$, within an LS like coupling scheme. The return to an LS skewed intermediate case for the heavier actinides is consistent with the atomic model of van der Laan and Thole [11], which has been used to explain the cross-sectional behavior of the lighter actinides [1,4].

It is useful to consider the possibility of phase specific variations of the XAS/EELS findings and thus the *n* value for Pu. As can be seen in Figures 3 and 4, within each technique, the results for α and δ are quite similar for the 5*d* to 5*f* transitions. Additionally, as shown in Figure 6, the $N_{4,5}$ electron-energy loss spectra for α and δ Pu are again similar [8]. The experimental data hence point towards the conclusion that for Pu *n* is less than 6 and greater than or equal to 5, either for the α or the δ phase. This does not rule out that there may be phase specific variations between the spectra, but these are small compared to the variation from element to element.
Thus, to summarize for Pu 5*f* occupation: From XAS and EELS, $5 \leq n < 6$, with $n \neq 6$.

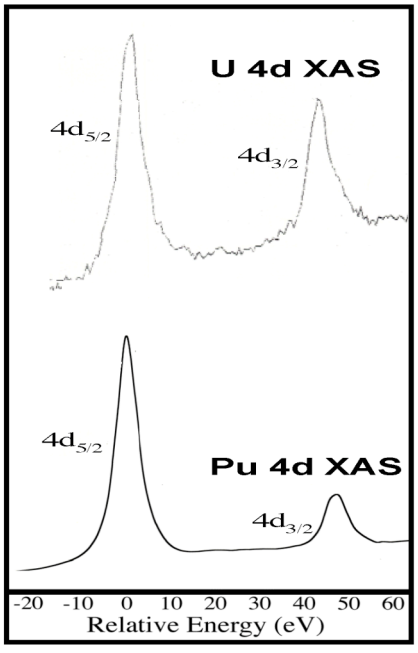

Figure 1.

The 4d to 5f XAS transition results for Pu [1] and U [6] are shown here. The photon energies were near 800 eV.

Simple Picture derived from the spectroscopic analysis

Result of non-magnetic calculation, including spin-orbit in the Pu 5f's

Result of anti-ferromagnetic calculation, including spin-orbit in the Pu 5f's

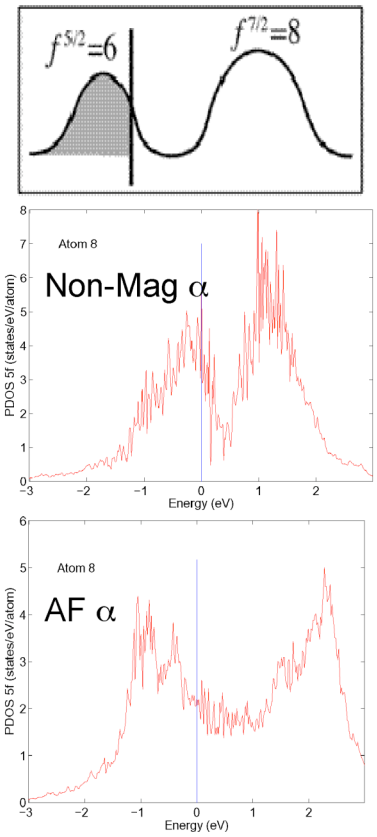

Figure 2.
The two lobed structure of the Pu 5*f* density of states is shown here. Top: the simple picture derived from the spectroscopic analysis. Middle: the result of non-magnetic calculation by Kutepov, including the spin-orbit splitting in the Pu 5*f* states. Bottom: the result of an anti-ferromagnetic calculation by Kutepov, including the spin-orbit splitting in the Pu 5*f* states. See Ref. 1 for the details concerning this figure.

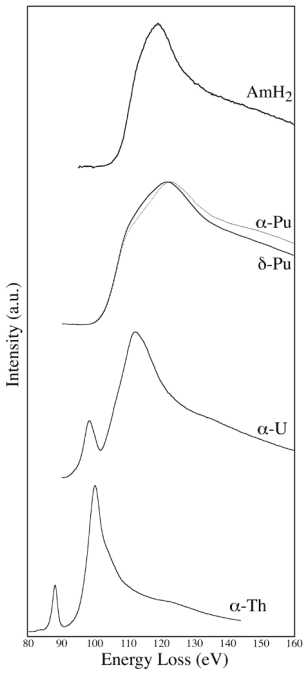

Figure 3.
The EELS spectra of the 5*d* to 5*f* transitions of Th (bottom), U, (second from bottom), Pu (second from top), and AmH_2 (top) are shown here. The Th, U, and Pu data are from Ref. 2. The AmH_2 data are from Ref. 8.

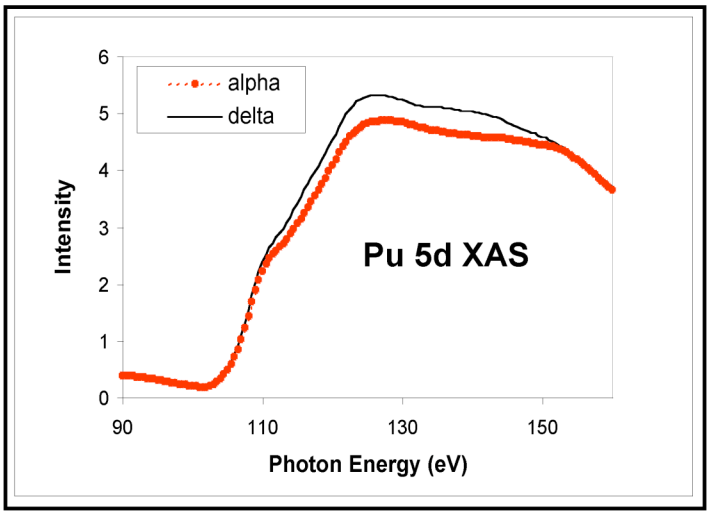

Figure 4.
The XAS data for the 5*d* to 5*f* transition in Pu is shown here. The spectra are taken from Ref. 2.

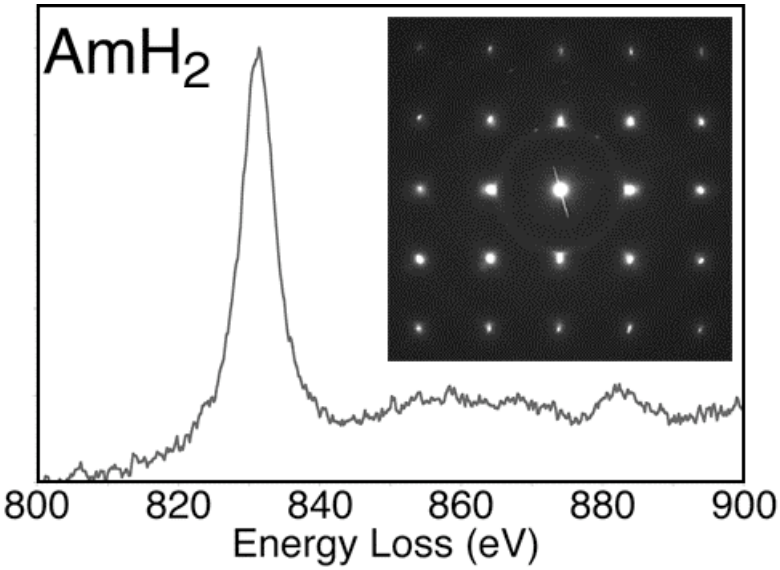

Figure 5.
The electron diffraction and EELS data for the 4*d* to 5*f* transition of Am, from an AmH_2 sample, is shown here. The data is taken from Ref. 8.

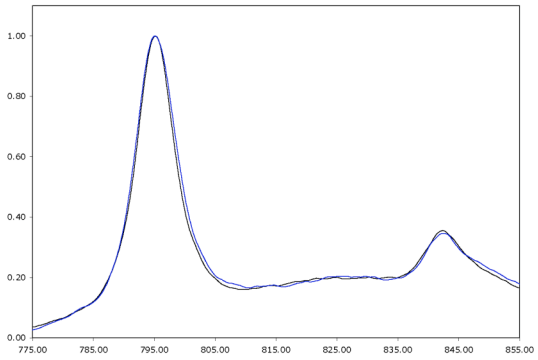

Figure 6.
The EELS data for the 4*d* to 5*f* transition in α and δ Pu is shown here. The spectra are taken from Ref. 8.

Acknowledgements

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